7 Supporting Processes: Effluent Treatment and Process Heaters

7.1 Effluents

Pretreatment Standards Apply to Effluents from Chemicals Manufacture

Effluents emitted during the production of chemicals consist primarily of waste waters from washing, crystallization, distillation towers, and cooling water. Much of this process water is recycled for reuse wherever possible. Wash waters containing solvents are usually sent to solvent recovery systems to recover water and control volatile solvent emissions. Wastewater containing hazardous or toxic components are often subjected to stripping to separate contaminants so water can be reused.

Limitations for toxic or hazardous compounds contained in wastewaters are given by the U.S. Environmental Protection Agency in 40 CFR, Chapter 1, which was originally promulgated in 1974 and has been revised several times since. These limitations apply to all facilities that manufacture organic chemicals, plastics, and synthetic fibers. Tables 7-1 and 7-2 provide the standards for effluents generated from the manufacture of commodity organic chemicals.

Table 7-1 Effluent Pretreatment Standards Organic Chemicals (micrograms/liter)

Effluent Characteristics	Maximum for One Day	Maximum Month Average
Benzene	134	57
Carbon Tetrachloride	380	142
Chlorobenzene	380	142
1,2,4-Trichlorobenzene	794	196
Hexachlorobenzene	794	196
1,2-Dichloroethane	574	180
1,1,1-Trichloroethane	59	22
Hexachloroethane	794	196
1,1-Dichloroethane	59	22
1,1,2-Trichloroethane	127	32
Chloroethane	295	110
Chloroform	325	111
1,2-Dichlorobenzene	794	196
1,3 Dichlorobenzene	380	142
1,4-Dichlorobenzene	380	142
1,1-Dichloroethylene	60	22
1,2-trans-Dichloroethylene	66	25

Source: CFR 40 Chapter 1, Part 414.

Table 7-2 Effluent Pretreatment Standards/Organic Chemicals (micrograms/liter)		
Effluent Characteristics	Maximum for One Day	Maximum Monthly Average
1,2-Dichloropropane	794	196
1,3-Dichloropropylene	794	196
Ethylene Benzene	380	142
Methylene Chloride	170	36
Methyl Chloride	295	110
Hexachlorobutadiene	380	142
Nitrobenzene	6402	2237
2-Nitrophenol	231	65
4-Nitrophenol	576	162
4,6-Dinitro-o-cresol	277	78
Tetrachloroethylene	164	52
Toluene	74	28
Trichloroethylene	69	26
Vinyl Chloride	172	97
Total Cyanide	1200	420
Total Lead	690	320
Total Zinc	2610	1050

Source: CFR 40 Chapter 1, Part 414.

A Diversity of Water Pretreatment Processes Are Available

Many chemical industry wastewaters must be pretreated prior to discharge to publicly owned treatment works (POTWs). The characteristics of these wastewaters vary considerably, depending on the chemical manufacturing process they came from. The water stream that exits from each process is likely to have unique pollutants, as well as temperatures, pressures, flow rates, and pH that are different from those of other process streams. The design and successful operation of wastewater treatment facilities on-site at the chemical plant requires continuous sampling and monitoring of these parameters. Some wastewaters will also go through several treatment stages before discharge to POTWs. Common treatment options are shown in Table 7-3.

There are a number of objectives in pretreating wastewater, including the following:

- Attaining a suitable pH for discharge
- Removing oil and grease
- Removing suspended solids
- Reducing/eliminating toxics and VOCs
- Removing heavy metals
- Equalizing wastewater flow

Achieving a **proper pH** is essential for meeting EPA'a effluent pretreatment standards and preventing problems in downstream treatment operations (e.g., biological treatment). Neutralization is required to attain a suitable pH. Acidic wastewaters are neutralized with lime, limestone, or caustic solutions. Alkaline (basic) wastewaters are neutralized with either sulfuric or hydrochloric acids, or carbon dioxide gas.

Oil and grease are generally easy to remove using mechanical separation or dissolved-air flotation, unless they are emulsified in the wastewater. In such cases coagulants are added to the water to coalescence the contaminants into large agglomerates that can be removed.

Suspended solids are present in wastewater in many forms and sizes, and the removal technique will depend on their classification (see Table 7-3). Large solids of 25 mm diameter or larger may interfere with downstream processes if they are not removed using screens. Grit such as sand and gravel are removed by sedimentation. Small particles of between 0.001 and 1 micrometer in diameter are referred to as colloids, and are removed by dissolved-air flotation or chemical coagulation.

Removal of metals is most commonly achieved by precipitating the metal out as an hydroxide using lime or caustic. Once metal hydroxides are precipitated, they must be coagulated or flocculated into larger, heavier particles that will settle out in a sedimentation pond, plate settler, or solids-contact clarifier. After separation, the remaining sludge is dewatered and landfilled (if not hazardous).

Volatile organic compounds (VOCs) are usually stripped by air or steam in packed towers. In thesetowers the air or steam flows countercurrently to the wastewater to remove the contaminant. Activated carbon columns may also be used to remove VOCs by absorption.

Table 7-3. Wastewater Treatment Options	
Waste Classification	**Option**
Acidic (low pH)	Neutralization with lime, limestone, or caustic solutions
Alkaline (high pH)	Neutralization with sulfuric or hydrochloric acids, or carbon dioxide gas
Oil and Grease	Mechanical skimming, dissolved -air flotation, chemical coagulants, carbon filters (soluble oils)
Suspended Solids (<1%)	Screening (bar or fine screens), gravity separation (sedimentation, chemical coagulation followed by sedimentation, dissolved-air flotation), granular media filtration, membrane filtration (microfiltration, ultrafiltration)
Suspended Solids (>1%)	Thickening (gravity thickening, dissolved-air floatation, centrifuging), dewatering (pressure, belt or vacuum filtration, centrifuging, sand-bed drying)
Heavy Metals	Hydroxide precipitation and dewatering, sedimentation, chemical oxidants (chlorine, ozone, hydrogen peroxide, potassium permanganate or chlorine dioxide), greensand filtration (iron, manganese)
Volatile Organic Compounds (VOCs)	Air or steam stripping, activated carbon absorption, incineration, biological treatment, ultrafiltration membranes, nanofiltration membranes, reverse osmosis
Non-Volatile Organic Compounds	Biological treatment (aerobic or anaerobic), ultrafiltration membranes, nanofiltration membranes, chemical oxidants with UV, reverse osmosis
Dissolved or Divalent Salts	Nanofiltration membranes, reverse osmosis
Inorganic Ions/Chlorine	Nanofiltration membranes, activated carbon filtration
Odors	Chemical oxidants
Bacterial/Viral Growth	Chemical oxidants, ultrafiltration membranes, nanofiltration membranes, reverse osmosis
COD	Chemical oxidants

Sources: CE 1991, CE 1992 BIO 1993, WWS 1999, Culligan 1999.

Biological treatments may be employed to destroy both volatile and non-volatile organic contaminants. In these systems the contaminants are consumed by microorganisms, which convert them to new cell matter, gases, or other inert products. These processes may take place with or without oxygen, although aerobic (with oxygen) processes are more common. If enough land is available, outdoor lagoons are often used for carrying out biological aerobic treatment of wastewaters.

The use of biological treatments has accelerated rapidly over the last decade, and is now applied to a much wider variety of organic contaminants. Biological waste-destruction systems are attractive to the chemical industry because of their low cost compared to conventional treatment alternatives. For example, DuPont conducted a study that indicated that controlling VOCs using biofiltration is at least 90 percent less expensive than using activated carbon or incineration processes, and costs 67 percent less than stripping processes (BIO 1993).

Chemical oxidants (e.g., chlorine, ozone, hydrogen peroxide, potassium permanganate, chlorine dioxide) may be used to destroy odors, control bacterial growth, reduce chemical oxygen demand (COD), and remove residual heavy metals from wastewater. Chemical oxidants are also sometimes combined with ultraviolet (UV) radiation for very thorough destruction of some organic contaminants. (Pretreatment descriptions: CE 1991, CE 1992, BIO 1993, WWS 1999, and Culligan 1999).

7.2 Process Heaters

Process Heaters Are Integrated into Every Chemical Process

Process heat from **direct-fired heaters** and **boiler steam** is necessary for nearly every process in the chemical plant. Steam, for example, is used for distillation, chemical reactions, heating, and drying. Most of the energy consumed in chemicals manufacture is used in heaters and boilers. Boilers and process heaters exist in a wide variety of designs, and a discussion of the large number of possible configurations is outside the scope of this report. However, typical combustion emission factors for these units are provided in Table 7-4.

In direct contact operations, the steam is used as a stripping medium or process fluid. In some applications steam may be used in vacuum ejectors to produce a vacuum. Steam is also used for drying, evaporation, and other processes where indirect heating is required.

Process heaters are used extensively to supply heat to raise the temperature of feed streams to a level necessary for chemical reaction or distillation. Maximum fluid temperatures reached by process heaters are about 950ºF (510ºC). Air preheaters are heat exchangers that recover heat in the flue gas by heating up combustion air. They are usually applied on large heaters in areas where NOx emissions are not a severe problem. Heaters with air preheaters produce much more NOx than do heaters that use air at ambient temperatures. A steam convection section can sometimes be used to duplicate the high efficiency obtained from a heater with an air preheater.

Furnaces are used in some cases for the incineration of effluent streams containing air pollutants, toxic chemicals, or hazardous wastes. In these specialized waste-destruction furnaces, temperatures can be much higher than in typical boilers. Excess heat from these systems may be recovered by heat exchange.

Waste heat recovery is an important component of many chemical processes. Reactions that are highly exothermic (e.g., heat-releasing) produce considerable amounts of heat that can be recovered as steam for export throughout the chemical plant. The production of sulfuric acid, for example, generates nearly 2000 Btu/lb of product in high pressure steam for export.

In many cases, however, the available waste heat is not recovered or is incompletely recovered, resulting in the loss of valuable heat energy. These heat losses throughout the chemical industry are estimated to be more than two quads annually, which is significant. Table 7-5 illustrates the potential energy content of waste heat streams in various chemical processes (PNNL 1984).

Table 7-4. Boiler Combustion Emission Factors By Fuel Type (lbs/million Btu)					
Fuel Type	**SO_x**	**NO_x**	**CO_2**	**Particulates**	**VOCs[a]**
Distillate Fuel	0.160	0.140	0.0361	0.010	0.002
Residual Fuel	1.700	0.370	0.0334	0.080	0.009
Other Oils	1.700	0.370	0.0334	0.080	0.009
Natural Gas	0.000	0.140	0.0351	0.003	0.006
LPG	0.000	0.208	0.0351	0.007	0.006
Propane	0.000	0.208	0.0351	0.003	0.006
Steam Coal	2.500	0.950	0.3044	0.720	0.005
Coke	2.500	0.950	0.3044	0.720	0.005
Electricity	1.450	0.550	0.1760[b]	0.400	0.004

a volatile organic compounds
b Electricity emissions of carbon dioxide are based on energy consumption for the national grid

Sources: **Particulates, SOx, NOx, VOCs** - U.S. Environmental Protection Agency, 1986, Compilation of Air Pollution Emission Factors, Vol 1, *Stationary Point and Area Sources, Supplement A*; *Supplement B* (September 1988); and 1995 updates.
CO_2 - U.S. Department of Energy. *Emissions of Greenhouse Gases in the United States, 1987-1992; Emissions of Greenhouse Gases in the United States, 1995.*

Table 7-5. Characteristics of Waste Heat Streams in Selected Chemical Sectors			
Chemical Process	**Million Btu/Ton of Product (Temperature in °F)**		
	Flue Gases	**Cooling Water**	**Other**
Caustic Soda (Sodium Hydroxide)	4.5 (120)	0.4 (180)	0.1
Chlorine	--	0.24 (190)	2.2
Soda Ash (Sodium Carbonate)	1.22 (400 to 500)	0.16	0.3
Styrene	0.6-0.7 (400 to 500)	29 (100 to120)	--
Ethylene	1.9 (400)	--	--
Ammonia	2.4 (400)	0.5 (100 to120)	0.43

Source: PNNL 1984.